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發明

全 1 頁

[51] Int.Cl <sup>06</sup>: C08K5/00

稱: 含有鹵化芳族二元醇和二鹵化伸烷基之縮合產物的乙烯芳族樹脂組成

物

[21]申請案號: 085101671

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[54]名

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#### [57]申請專利範圍:

- 1.一種阻燃熱塑型組成物,其包含:
  - (a)基於組成物總量之60至97重量百分 比之乙烯芳族樹脂,及
  - (b)基於組成物總量之3至40重量百分 比之阻燃劑,該阻燃劑為以下通式之 化合物:

$$R_i \cdot O \xrightarrow{R_i} X_i \xrightarrow{R_i} X_i \xrightarrow{R_i} O \cdot R_i \cdot O \xrightarrow{X_i} X_i \xrightarrow{X_i} X_i \xrightarrow{R_i} X_i \xrightarrow{R_i} O \cdot R_i$$

其中各個 R<sup>6</sup> 分別為 C<sub>1</sub> 至 C<sub>18</sub> 烷基,各個 R<sup>8</sup> 分別選自溴、氯、氫及 C<sub>1</sub>至 C<sub>5</sub>烷基,但其前題是各個雙酚部份之至少一個 R<sup>8</sup> 基團為溴、各個 R<sup>7</sup> 為具有 1 至 18 個碳原子之二價基團、各個 Y<sup>1</sup> 分別選自 -O-、-S-、-SO<sub>2</sub>、-SO-、-CO-、具有 1 至 10 個碳原子之伸烷基及亞烷基,且 n<sup>2</sup> 選自 1至 12。

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- 2.如申請專利範圍第1項之組成物,其中,該組成物進一步包含丙烯腈-二烯-乙烯芳族接枝共聚物。
- 3.如申請專利範圍第2項之組成物、其中、該接枝共聚物為內烯腈-丁二烯-苯乙烯接枝共聚物。
  - 4.如申請專利範圍第1項之組成物,其中,該阻燃劑係以以下之通式表示:

其中n²選自1至12。

- 5.如申請專利範圍第1項之組成物、共中,該組成物進一步包含1至15重量百分比之銻化合物。
- 15. 6.如申請專利範圍第1項之組成物、其中,該乙烯芳族樹脂是經衝擊改質之 本乙烯聚合物。

# PATENT BULLETIN OF REPUBLIC OF CHINA (TRANSLATION)

Patent No.: 442523 Date: 23 June 2001

Invention

Pages: 1

Int. Cl.<sup>7</sup> : C08K5/00

Title of Invention: Vinyl aromatic resin compositions containing condensation product

of halogenated aromatic diol and an alkylene dihalide

Application No.: 085101671 Filing Date: 10 February 1996

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#### Claims:

1. A flame retardant thermoplastic composition comprising: (a) a vinyl aromatic resin present at a level of from 60 to 97 percent by weight based on the total weight of the composition, and

(b) a flame retardant present at a level of from 3 to 40 percent by weigh based on the total weight of the composition, said flame retardant being of the general formula:

$$R^{1} - Q = R^{1}$$
 $R^{1}$ 
 $R^{1}$ 
 $R^{2}$ 
 $R^{3}$ 
 $R^{4}$ 
 $R^{4}$ 
 $R^{4}$ 
 $R^{4}$ 
 $R^{4}$ 
 $R^{5}$ 
 $R^{5}$ 

wherein each  $R^6$  is independently a  $C_1$  to  $C_{18}$  alkyl radical, each  $R^8$  is independently selected from the group consisting of bromine, chlorine, hydrogen and  $C_1$  to  $C_5$  alkyl radicals, provided that at least one  $R^8$  of each bisphenol moiety is a bromine, each  $R^7$  is a divalent radical selected from the group consisting of divalent radicals having from 1 to 18 carbon atoms, each  $Y^1$  is independently selected from the group consisting -O-, -S-, -SO<sub>2</sub>-, -SO-, -CO-, and alkylene and alkylidene radicals having from 1 to 10 carbon atoms, and  $n^2$  is selected from 1 to 12.

- 2. The composition of claim 1 wherein said composition further comprises a vinyl cyanide-diene-vinyl aromatic graft copolymer.
- 3. The composition of claim 2 wherein said graft copolymer is an acrylonitrile-butadiene-styrene graft copolymer.

4. The composition of claim 1 wherein said flame retardant is represented by the following general formula:

wherein n<sup>2</sup> is selected from 1 to 12.

- 5. The composition of claim 1 wherein said composition further comprises from 1 to 15 percent by weight of an antimony compound.
- 6. The composition of claim 1 wherein said vinyl aromatic resin is an impact modified styrene polymer.

## Vinyl aromatic resin compositions containing condensation product of halogenated aromatic diol and an alkylene dihalide

经工程的证据中国的主义在职,在一个大小的工作,但如果,如此的主要,如此的主题的,但是是是是一个大小的工作的工作,也不是一个人的工作,但是一个人的工作,也不是一个

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- European:

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Abstract of TW 442523 (B)

A flame retardant thermoplastic composition is provided containing a vinyl aromatic resin and a flame retardant. The flame retardant is an oligomeric condensation product of a halogenated aromatic diol and an alkylene dihalide composition which is preferably an admixture of an alkyl monohalide and an alkylene dihalide. The compositions are useful for making molded articles for automotive parts and for business machine housings. The composition exhibit no bloom, good thermal color stability, and good resistance to ultraviolet light.

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🔁 AU707802 (B2)

**AU5190396** (A)

more >>



## United States Patent [19]

#### Kulich et al.

[52]

[11] Patent Number: 5,559,172

**Date of Patent:** [45]

Sep. 24, 1996

[54]	CONTAIN OF HALO	ROMATIC RESIN COMPOSITIONS NING CONDENSATION PRODUCT DGENATED AROMATIC DIOL AND VLENE DIHALIDE
[75]	Inventors:	Donald M. Kulich, Marietta, Ohio; Thomas B. Cleveland, Parkersburg, W. Va.; Enrico J. Termine, West Lafayette; Arthur G. Mack, Lafayette, both of Ind.
[73]	Assignee:	General Electric Company, Pittsfield, Mass.
[21]	Appl. No.:	439,014
[22]	Filed:	May 11, 1995
[51]	Int. Cl.6.	C08K 5/06; C08K 5/36;

U.S. Cl. ...... 524/155; 524/167; 524/373;

[58] Field of Search ...... 524/373, 411,

C08K 5/02

524/411; 524/412

524/412, 155, 167

#### [56] References Cited

#### U.S. PATENT DOCUMENTS

4,032,508	6/1977	Anderson	524/373
5,414,046	5/1995	Davis	525/132
5,420,183	5/1995	Arena et al	524/373

Primary Examiner-Kriellion S. Morgan

#### [57] **ABSTRACT**

A flame retardant thermoplastic composition is provided containing a vinyl aromatic resin and a flame retardant. The flame retardant is an oligomeric condensation product of a halogenated aromatic diol and an alkylene dihalide composition which is preferably an admixture of an alkyl monohalide and an alkylene dihalide. The compositions are useful for making molded articles for automotive parts and for business machine housings. The composition exhibit no bloom, good thermal color stability, and good resistance to ultraviolet light.

27 Claims, No Drawings

Typically, the dihydric phenols utilized in the preparation of the polycarbonate resins may be represented by the general formula

HO 
$$(R^1)_{a_1}$$
 OH.

wherein R, R<sup>1</sup>, n, n<sup>1</sup>, W and b are as defined hereinafore. Some illustrative non-limiting examples of dihydric phenols falling within the scope of Formula II include 2,2-bis(4hydroxyphenyl) propane (bisphenol-A); 2,2-bis(3,5-dibromo-4-hydroxyphenyl) propane; 2,2-bis(3,5-dimethyl-4hydroxyphenyl) propane; 2,2-bis(3-bromo-5-methyl-4- 15 hydroxyphenyl) propane; 1,1-bis(4-hydroxyphenyl) cyclohexane; 1,1-bis(4-hydroxyphenyl) cyclododecane; 1,1bis(3,5-dimethyl-4-hydroxyphenyl) cyclododecane; 1,1bis(4-hydroxyphenyl) decane; 1,4-bis(4-hydroxyphenyl) butane; bis(4-hydroxyphenyl) methane; 4,4'-thiodiphenol; 20 and bis(4-hydroxyphenyl) ether.

Other phenols which are useful are described in U.S. Pat. Nos. 2,998,835, 3,028,365 and 3,334,154, all of which are incorporated herein by reference.

The carbonate precursor may be a carbonyl halide, a 25 carbonate ester, or a bishaloformate. The carbonyl halides may be carbonyl bromide, carbonyl chloride, or mixtures thereof. The carbonate esters may be diphenyl carbonate; di(halophenyl) carbonates such as di(-bromophenyl) carbonate, di(chlorophenyl) carbonate, and di(tribromophenyl) carbonate; di(alkylphenyl) carbonates such as di(tolyl) carbonate; di(naphthyl) carbonate; chlorophenyl chloronaphthyl carbonate; and phenyl tolyl carbonate. The bishaloformates that can be used include the bishaloformates of dihydric phenols such as the bischloroformates of bisphenol-A and 35 hydroquinone; and the bishaloformates of glycols such as the bischloroformates of ethylene glycol, neopentyl glycol, and polyethylene glycol. The preferred carbonate precursor is carbonyl chloride, also known as phosgene.

Among the processes used for the preparation of the 40 polycarbonates are the pyridine process, the interfacial polymerization process, transesterification, and melt polymerization. A convenient process for the preparation of the polycarbonate resins is the interfacial polymerization process. This process utilizes two different solvent media which 45 are immiscible. One solvent medium is an aqueous basic medium. The other solvent medium is an organic medium such as methylene chloride which is immiscible with said aqueous medium. Also employed in the interfacial polymerization process are molecular weight regulators which control the chain length or molecular weight of the polycarbonate by a chain terminating mechanism, and catalysts. The molecular weight regulators are well known in the art and include, but are not limited to, phenyl itself, p-tertiarybutyl phenol, and chroman-I. The catalysts are also well known in 55 the art and include, but are not limited to, tertiary amines such as triethylamine, quaternary ammonium compounds such as tetraethylammonium bromide, and quaternary phosphonium compounds such as n-butyltriphenyl phospho-

Also included within the scope of the term polycarbonates are the randomly branched thermoplastic polycarbonates wherein a branching agent, which is generally a polyfunctional aromatic compound, is reacted with a dihydric phenol and the carbonate precursor. These polyfunctional aromatic 65 compounds are used in minor amounts, i.e., amount effective to provide branching, and contain at least three functional

groups which may be carboxyl, hydroxyl, carboxylic anhydride, haloformyl, and mixtures thereof. Some illustrative non-limiting examples of these aromatic polyfunctional compounds which may be employed as branching agents include trimellitic anhydride, trimellitic acid, trimellity trichloride, 4-chloroformyl phthalic anhydride, pyromellitic acid, pyromellitic dianhydride, mellitic acid, mellitic anhydride, trimesic acid, and benzophenonetetracarboxylic acid.

The copolyester-carbonate resins are well known in the art and are described along with methods for their preparation in U.S. Pat. Nos. 3,169,121; 4,238,596; 4,156,069 and 4,238,597, all of which are incorporated herein by reference.

Briefly stated the high molecular weight thermoplastic aromatic copolyester-carbonates comprise recurring carbonate groups, carboxylate groups, and aromatic carbocylic groups in the polymer chain in which at least some of the carbonate groups and at least some of the carboxylate groups are bonded directly to the ring carbon atoms of the aromatic carbocyclic groups. These copolyester-carbonates contain ester bonds and carbonate bonds in the chain, wherein the amount of the ester bonds is in the range of from about 25 to about 90 mole percent, preferably from about 35 to about 80 mole percent. For example, 5 moles of bisphenol-A reacting completely with 4 moles of isophthaloyl dichloride and one mole of phosgene would give a copolyester-carbonate of 80 mole percent ester bonds.

These copolyester-carbonates may be readily prepared by the interfacial polymerization process by the reaction of (i) at least one dihydric phenol, (ii) a carbonate precursor, and (iii) an ester precursor. The dihydric phenols and the carbonate precursors are of the type described hereinafore. The ester precursor may be a difunctional carboxylic acid or, preferably, its ester forming reactive derivative such as an acid dihalide, e.g., isophthaloyl dichloride, terephthaloyl dichloride, and mixtures thereof. Some useful difunctional acids are set forth in U.S. Pat. No. 3,169,121. The polyesters may be either aliphatic aromatic, or aliphatic-aromatic in character. The polyesters are characterized in that they have recurring ester units in the polymer chain, i.e., carboxylate groups bonded to a carbon atom of a hydrocarbon or substituted hydrocarbon radical.

The preferred polyesters for use in the instant invention generally contain at least one recurring structural unit represented by the general formula:

$$\begin{array}{cccc}
O & O & & & & \\
\parallel & \parallel & & \parallel & & \\
+O-R^2O-C-R^3-C+ & & & & \\
\end{array}$$

wherein  $\mathbb{R}^2$  and  $\mathbb{R}^3$  are independently selected from divalent hydrocarbon radicals or substituted divalent hydrocarbon radicals.

In the case of aliphatic polyesters both R2 and R3 are independently selected from divalent aliphatic hydrocarbon radicals or substituted divalent aliphatic hydrocarbon radicals. The divalent aliphatic hydrocarbon radicals include the alkylene, alkenylene, alkylidene, cycloalkylene, cycloalkylidene, and cycloalkenylene radicals. Preferred alkylene radicals are those containing from 2 to about 20 carbon atoms. The preferred alkylidene radicals are those containing from 1 to about 20 carbon atoms. The preferred alkenylene radicals are those containing from 2 to about 20 carbon atoms. The preferred cycloalkylene, cycloalkylidene, and cycloalkenylene radicals are those containing from about 4 to about 8 ring carbon atoms. The substituted divalent aliphathic hydrocarbon radicals are those divalent aliphatic hydrocarbon radicals described above which contain at least one substituent group, preferably from one to about three substituent groups. The preferred substituent groups are the halogens, nitro groups, and amino groups.

weight percent polyester resin are more preferred. Quite useful compositions are those that contain from about 20 to about 60 weight percent aromatic carbonate resin and from about 60 to about 20 weight percent polyester resin. Weight percent aromatic carbonate resin is based on the total amounts of aromatic carbonate resin and polyester resin present in the compositions. Likewise, weight percent polyester is based on the total amounts of the polyester resins and aromatic carbonate resin present in the instant compositions, i.e., polyester/aromatic carbonate blends.

The polyphenylene ether (PPE) resins are generally well-known in the art, and are described, for example, in U.S. Pat. Nos. 3,306,874; 3,306,875; and 3,432,469 of Allan Hay; U.S. Pat. Nos. 3,257,357 and 3,257,358 of Gelu Stamatoff; U.S. Pat. No. 4,806,602 of Dwain M. White et al.; and U.S. Pat. No. 4,806,297 of Sterling B. Brown et al., all incorporated herein by reference. Both homopolymer and copolymer polyphenylene ethers are within the scope of this invention

The preferred PPE resins are homo- and copolymers which comprise a plurality of structural units of the formula

$$Q^2$$
  $Q_1$   $Q_1$ 

wherein each  $Q^1$  is independently halogen, primary or 30 secondary lower alkyl, phenyl, haloalkyl, aminoalkyl, hydrocarbonoxy, or halohydrocarbonoxy, wherein at least two carbon atoms separate the halogen and oxygen atoms; and each  $Q^2$  is independently hydrogen, halogen, primary or secondary lower alkyl, phenyl, haloalkyl, hydrocarbonoxy 35 or halohydrocarbonoxy as defined for  $Q^1$ .

Examples of suitable primary lower alkyl groups are methyl, ethyl, n-propyl, n-butyl, isobutyl, n-amyl, isoamyl, 2-methylbutyl, n-hexyl, 2,3-dimethylbutyl, 2-, 3- or 4-methylpentyl, and the corresponding heptyl groups. Examples 40 of secondary lower alkyl groups are isopropyl, sec-butyl and 3-pentyl. Preferably, any alkyl radicals are straight chain, rather than branched. Often, each Q¹ is alkyl or phenyl, especially C¹—4 alkyl, and each Q² is hydrogen. Especially preferred polyphenylene ethers will be comprised of units 45 derived from 2,6-dimethyl phenol. Also preferred in some instances are PPE copolymers comprised of units derived from 2,6-dimethyl phenol and 2,3,6-trimethyl phenol.

The PPE resins may contain certain moieties which modify properties such as molecular weight, melt viscosity, 50 or impact strength. For example, vinyl monomers and vinylaromatic compounds may be grafted onto the PPE polymer, as described, for example, in the application of Sterling B. Brown et al., Attorney Docket Number RD-19372, U.S. Ser. No. 351,903, filed May 15, 1989, the entire contents of 55 which are incorporated herein by reference.

As another example, coupled PPE polymers may also be used, in which the coupling agent is reacted with hydroxy groups of two PPE chains to produce a higher molecular weight polymer.

The PPE resins of this invention generally have a weight average molecular weight of about 20,000 to 80,000, as determined by gel permeation chromatography.

Furthermore, they can be prepared by methods known in the art: for example, oxidative coupling of an appropriate 65 monohydroxyaromatic compound in the presence of a catalyst based on copper, manganese, or cobalt. The preferred thermoplastic resin is a rubber modified monovinylidene aromatic such as a vinyl aromatic-vinyl cyanide-diene rubber graft copolymer.

Rubber modified monovinylidene aromatic resins comprising (a) a rubber modified monovinylidene aromatic graft copolymer and (b) an ungrafted rigid copolymer, are generally prepared by graft polymerization of a mixture of a monovinylidene aromatic monomer and one or more comonomers in the presence of one or more rubbery polymeric substrates. Depending on the amount of rubber present, a separate matrix or continuous rigid phase of ungrafted rigid (co)polymer may be simultaneously obtained along with the rubber modified monovinylidene aromatic graft polymer. The resins may also be produced by blending a rigid monovinylidene aromatic copolymer with one or more rubber modified monovinylidene aromatic graft copolymers. Typically, the rubber modified resins comprise the rubber modified graft copolymer at a level of from 5 to 100 percent by weight based on the total weight of the resin, more preferably from 10 to 95 percent by weight thereof, more preferably 20 to 90 percent by weight thereof, and most preferably from 15 to 85 percent by weight thereof; and the rubber modified resin comprises the ungrafted rigid polymer at a level of from 0 to 95 percent by weight based on the total weight of the resin, more preferably from 5 to 90 percent by weight thereof, more preferably from 10 to 80 percent by weight thereof and most preferably from 15 to 85 percent by weight thereof.

Monovinylidene aromatic monomers which may be employed include styrene, alpha-methyl styrene, halostyrenes i.e. dibromostyrene, mono or di alkyl, alkoxy or hydroxy substitute groups on the nuclear ring of the monovinylidene aromatic monomer i.e. vinyl toluene, vinylxylene, butylstyrene, parahydroxystyrene or methoxystyrene or mixtures thereof. The monovinylidenearomatic monomers utilized are generically described by the following formula:

$$\begin{array}{c|c} X & R^4 \\ X & C = C \\ X & X \end{array}$$

wherein X is selected from the group consisting of hydrogen, alkyl groups of 1 to 5 carbon atoms, cycloalkyl, aryl, alkaryl, aralkyl, alkoxy, aryloxy, and halogens.  $R^4$  is selected from the group consisting of hydrogen, alkyl groups of 1 to 5 carbon atoms and halogens such as bromine and chlorine. Examples of substituted vinylaromatic compounds include styrene, 4-methylstyrene, 3,5-diethylstyrene, 4-n-propylstyrene,  $\alpha$ -methylstyrene,  $\alpha$ -methyl vinyltoluene,  $\alpha$ -chlorostyrene,  $\alpha$ -bromostyrene, dichlorostyrene, dibromostyrene, tetrachlorostyrene, mixtures thereof and the like. The preferred monovinylidene aromatic monomers used are styrene and/or  $\alpha$ -methylstyrene.

Comonomers which may be used with the monovinylidene aromatic monomer includes acrylonitrile, methacrylonitrile,  $C_1$  to  $C_8$  alkyl or aryl substituted acrylate,  $C_1$  to  $C_8$  alkyl, aryl or haloaryl substituted methacrylate, acrylic acid, methacrylic acid, iraconic acid, acrylamide, N-substituted acrylamide or methacrylamide, maleic anhydride, maleimide, N-alkyl, aryl or haloaryl substituted maleimide, glycidyl (meth)acrylates, hydroxy alkyl (meth)acrylates or mixtures thereof. The acrylonitrile, substituted acrylonitrile, or acrylic acid esters are described generically by the following formula:

The ungrafted rigid copolymers are known and may be prepared by radical polymerisation, in particular by emulsion, suspension, solution or bulk polymerisation. They preferably have number average molecular weights of from 20,000 to 200,000.

The number average molecular weight of the grafted rigid superstrate of the monovinylidene aromatic resin is designed to be in the range of 20,000 to 350,000. The ratio of monovinylidene aromatic monomer to the second and optionally third monomer may range from 90/10 to 50/50 10 preferably 80/20 to 60/40. The third monomer may optional replace 0 to 50% of one or both of the first and second monomers.

These rubber modified monovinylidene aromatic graft polymers may be polymerized either by mass, emulsion, 15 suspension, solution or combined processes such as bulk-suspension, emulsion-bulk, bulk-solution or other techniques well known in the art. Furthermore, these rubber modified monovinylidene aromatic graft copolymers may be produced either by continuous, semibatch or batch pro- 20 cesses.

The compositions preferably contain the flame retardant at a level of from 3 to 40 percent by weight based on the total weight of the composition, more preferably from 7 to 25 percent by weight thereof, and most preferably from 12 to 20 25 percent by weight thereof.

The flame retardant is a condensation product of a halogenated aromatic diol, preferably brominated aromatic diol, and an alkylene dihalide composition. The brominated aromatic diol is preferably a brominated bisphenol A, and is 30 more preferably tetrabromo bisphenol A. The alkylene dihalide composition is preferably a mixture of a C<sub>1</sub>-C<sub>18</sub> (one to eighteen carbon atoms in the alkyl moiety) alkyl monohalide and a C<sub>1</sub>-C<sub>18</sub> alkylene dihalide. The C<sub>1</sub>-C<sub>18</sub> alkyl monohalide is preferably a C<sub>1</sub>-C<sub>4</sub> alkyl bromide, and more 35 preferably methyl bromide. The  $C_1$ - $C_{18}$  alkylene dihalide is preferably a C<sub>1</sub>-C<sub>4</sub> alkylene bromide, and more preferably is ethylene dibromide. The alkylene dihalide composition preferably comprises from 5 to 95 percent by weight alkyl monohalide based on the total weight of the alkylene diha- 40 lide composition, more preferably from 10 to 40 percent by weight thereof, and most preferably from 20 to 35 percent by weight thereof; and preferably comprises from 5 to 95 percent by weight alkylene dihalide based on the total weight of the alkylene dihalide composition, more prefer- 45 ably from 60 to 90 percent by weight thereof, and most preferably from 65 to 80 percent by weight thereof. The alkyl monohalide and the alkylene dihalide are preferably present in the alkylene dihalide composition in a respective molar ratio of between 1:9 and 2:1, more preferably between 50 1:5 and 1.5:1, and most preferably between 1:3 and 1:1. The oligomeric flame retardant preferably has a number average molecular weight of between 1000 g/mole and 8000 g/mole, more preferably between 1300 g/mole and 6000 g/mole, and most preferably between 1500 g/mole and 3000 g/mole. The 55 alkyl monohalide is preferably of the formula

wherein X<sup>2</sup> is a halogen preferably selected from the group consisting of chlorine and bromine, and most preferably is bromine; and  $R^6$  is a (branched or unbranched)  $C_1$ – $C_{18}$  alkyl radical, preferably a  $C_1$ – $C_4$  alkyl radical, and is more preferably selected from the group consisting of methyl and ethyl radicals. The alkylene dihalide is preferably of the formula:

wherein  $X^2$  is as defined above; and  $R^7$  is an alkylene divalent radical having from  $C_1$ – $C_{18}$  carbon atoms, preferably from  $C_1$ – $C_6$  carbon atoms, and is most preferably selected from the group consisting of ethylene and divalent radicals.

The halogenated aromatic diol, preferably brominated aromatic diol, is more preferably a brominated bisphenol of the formula

wherein each R<sup>8</sup> is independently selected from the group consisting of a hydrogen atom, a chlorine atom, a bromine atom and an alkyl group containing from 1 to 5 carbon atoms provided that at least one R<sup>8</sup> group is a chlorine or bromine atom and preferably is a bromine atom; and wherein Y<sup>1</sup> represents a single bond or a divalent radical selected from the group consisting of —O—, —S—, —SO<sub>2</sub>—, —SO—, —CO—, alkylene and alkylidene groups containing 1 to 10 carbon atoms, and oxygen-, silicon-, sulfur- or nitrogencontaining aliphatic hydrocarbon radicals such as —OR<sup>9</sup>O—, —OR<sup>9</sup>OR<sup>9</sup>O—, —SR<sup>9</sup>S—, —SR<sup>9</sup>SR<sup>9</sup>S—, OSiR<sup>9</sup><sub>2</sub>O—, —OSiR<sup>9</sup><sub>2</sub>OSiR<sup>9</sup><sub>2</sub>O—, —O<sub>2</sub>CR<sup>9</sup>CO<sub>2</sub>, —CO<sub>2</sub>R<sup>9</sup>O<sub>2</sub>C—, —SOR<sup>9</sup>SO—, —SO<sub>2</sub>R<sup>9</sup>SO<sub>2</sub>—wherein R<sup>9</sup> is a C<sub>1</sub>-C<sub>10</sub> divalent aliphatic hydrocarbon radicals. Preferably at least 4 of the R<sup>8</sup> groups of the above diol are bromine. Preferably Y<sup>1</sup> is a C<sub>3</sub> radical. The preferred brominated bisphenol is tetrabromo bisphenol A, which may be represented by the general formula

and more preferably

The flame retardant may be represented by the general formula:

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Example 4 involved the replacement of the ABS of example 1 with a bisphenol A polycarbonate/ABS blend, and yielded a UL-94 rating of V-0 at 60 mil, a notched Izod of 9.7 ft-lb/in., and a melt viscosity of 1405 poise at 1000/s and 500° F.

We claim:

1. A vinyl aromatic resin composition comprising from 3 to 40 percent by weight of a flame retardant which is an oligomeric condensation product of a halogenated aromatic diol and an alkylene dihalide composition comprising alkylene dihalide.

2. The composition of claim 1 wherein said composition comprises a vinyl cyanide-diene-vinyl aromatic graft copolymer.

3. The composition of claim 2 wherein said graft copolymer is an acrylonitrile-butadiene-styrene graft copolymer.

4. The composition of claim 1 wherein said flame retardant is the condensation product of tetrabromobisphenol A, methyl bromide and ethylene dibromide.

5. The composition of claim 1 wherein said flame retardant is represented by the general formula:

8. The composition of claim 6 wherein said flame retardant is present at a level of from 7 to 25 percent by weight based on the total weight of the composition.

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9. The composition of claim 6 wherein said flame retardant is present at a level of from 12 to 20 percent by weight based on the total weight of the composition.

10. The composition of claim 6 wherein said composition further comprises from 1 to 15 percent by weight of an antimony compound.

11. The composition of claim 1 wherein said composition further comprises from 1 to 15 percent by weight of an antimony compound.

12. The composition of claim 1 further comprising an aromatic polycarbonate resin.

13. The composition of claim 1 further comprising a polyalkylene terephthalate resin.

14. The composition of claim 1 further comprising a polyphenylene ether resin.

15. The composition of claim 1 wherein said flame retardant is an oligomeric condensation product of a bromi-

wherein each  $R^6$  is independently a  $C_1$  to  $C_{18}$  alkyl radical, each  $R^8$  is independently selected from the group consisting of bromine, chlorine, hydrogen and  $C_1$  to  $C_5$  alkyl radicals, provided that at least one  $R^8$  of each bisphenol moiety is a bromine, each  $R^7$  is a divalent radical selected from the group consisting of divalent radicals having from 1 to 18 carbon atoms, each  $Y^1$  is independently selected from the group consisting  $O_7$ ,  $S_7$ , and alkylene and alkylidene radicals having from 1 to 10 carbon atoms, and  $S_7$  is selected from 1 to 12.

6. A flame retardant thermoplastic composition comprising:

(a) a vinyl aromatic resin present at a level of from 60 to 97 percent by weight based on the total weight of the composition, and

(b) a flame retardant present at a level of from 3 to 40 percent by weigh based on the total weight of the composition, said flame retardant being of the general formula:

nated aromatic diol and an alkylene dihalide composition comprising an alkyl monohalide and an alkylene dihalide.

16. The composition of claim 1 wherein said vinyl aromatic resin is an impact modified styrene polymer.

17. The composition of claim 1 wherein said oligomeric condensation product is substantially free of reactive end groups.

18. The composition of claim 1 wherein said oligomeric condensation product comprises alkyl end groups.

19. The composition of claim 1 wherein said oligomeric condensation product is an halogenated polyether.

20. The composition of claim 1 wherein said halogenated aromatic diol is a brominated aromatic diol.

21. The composition of claim 1 wherein said oligomeric condensation product has a number average molecular weight of between 1000 g/mole and 8000 g/mole.

$$CH_3-O \longrightarrow Br O \longrightarrow CH_2-CH_2-O \longrightarrow Br O \longrightarrow CH_2$$

wherein n<sup>2</sup> is selected from 1 to 12.

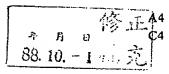
7. The composition of claim 6 wherein  $n^2$  is selected from 1 to 5.

22. The composition of claim 1 wherein said oligomeric condensation product has a number average molecular weight of between 1300 g/mole and 6000 g/mole.

## 公告本

附件三:第 85101671 號專利申請案中文說明書修正頁 民國 88 年 10 月呈

申請	日期		85	年	2	月	10	日
案	號			8516	0167	1		
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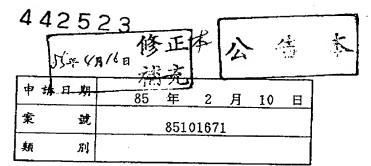


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訂

( x	以上各欄由	本局填註)
	有	<b>参明</b> 專利說明書 新型 專利說明書
· 發明	中文	含有鹵化芳族二元醇和二鹵化伸烷基之縮合産物的乙烯芳族樹脂維成物
新型	英文	Vinyl aromatic resin compositions containing condensation product of halogenated aromatic diol and an alkylene dihalide
	姓 名	(1) 湯姆士・克里夫蘭 Cleveland, Thomas Benson ② 唐諾・古利奇 Kulich, Donald Michael (3)安瑞克・特選 Termine, Enrico J.
發明 .	図 籍	(1) 美國 (2) 美國 (3) 美國 (1) 美國西維吉尼亞州・帕克斯堡・第十街三一六 號
二、創作人	住、居所	316 10th Street, Parkersburg, West Virginia 26101, US ② 美國俄亥俄州・瑪利塔・郵政三八六A號七 Rt. 7 Box 386A, Marietta, Ohio 45750, USA
		(3) 美國印地安那州・西拉法雅特・班特布克巷二 八四一號 2841 Bentbrook Lane, West Lafayette, Indiana 47906, U
	姓 名 (名稱)	(1) 通用電機股份有限公司 General Electric Company
	國 籍	(1) 美國
三、申請人	住、居所(事務所)	(1) 美國紐約州·斯克奈塔第河濱路一號 1 River Road, Schenectady, N.Y. 12345, USA
	代表人姓名	



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線

	(以上	各棚由									
		) 	發新	明型	專	利	説	明	書		
一、發明 名 新型 名	中	文 ———		-							
新型	英	文									
	姓	名	40	亞特	・馬克	Mack,	Arthur	G.			
	幺	藉	<b>(4</b> )	英國							
二、發明人	住、	居所	(4)	五〇.	一號				克貝里巷 , [ndia	五 na 47905,	USA
	姓 (名:	名稱)						R - 1		· · · · · · · · · · · · · · · · · · ·	
	國	籍									
三、申请人	住、人(事務	居所)									
	代表姓	人名									
											ĺ

承辦人代碼: 大 類: IPC分類:

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本案已向:

美國

國(地區) 申請專利,申請日期:

案號:

,□有 □無主張優先權

**図無主張優先權** 

(請先閱讀背面之注意事項再填寫本頁各欄)

線

有關做生物已寄存於:

, 寄存日期:

1995 年 5 月 11 日 08/439,014

, 寄存號碼:

經濟部中央標準局員工消費合作社印製

線

四、中文發明摘要(發明之名稱:

含有鹵化芳族二元醇和二鹵化伸烷基之縮合產物的乙烯芳族樹脂組成物

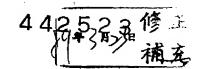
在此提供一種含有乙烯芳族樹脂與阻燃劑之阻燃性熟塑型組成物。該阻燃劑爲鹵化芳族二元醇與二鹵化伸烷基組成物(以單鹵化烷與二鹵化伸烷基之掺合物爲較佳)之低聚性縮合產物。該組成物在汽車零件及商用機械護罩之模製物件的製造上極具用途。該組成物不會白化、具有良好之遇熱顏色安定性、及良好的抗紫外光性。

#### 英文發明摘要(發明之名稱:

Vinyl aromatic resin compositions containing condensation product of halogenated aromatic diol and an alkylene dihalide

A flame retardant thermoplastic composition is provided containing a vinyl aromatic resin and a flame retardant flame retardant. The oligomeric condensation product of a halogenated aromatic diol and an alkylene dihalide composition of alkyl admixture which is preferably an alkylene dihalide. monohalide and an compositions are useful for making molded articles automotive parts and for business machine The composition exhibit no bloom, good housings. thermal color stability, and good resistance to ultraviolet light.

線



附件 2:第 85101671 號專利申請案中文說明書修正頁 民國 89 年 3 月呈

公告本

五、發明説明

發明背景

發明範疇

本發明係關於乙烯芳族樹脂組成物並且更特定言之係關於阻燃性乙烯芳族樹脂組成物。

#### 相關技藝的敘述

溴化阻燃劑及其用於阻燃乙烯芳族樹脂(例如丙烯腈一丁二烯一苯乙烯(ABS)接枝共聚物)的用途早爲人所習知。更特定言之,ABS接枝共聚組成物中使用經溴化之雙酚A即爲一例。然而,此種阻燃組成物因爲阻燃劑的掺入而有以下之一或多種缺點,即(a)不良的紫外光安定性,(b)不良的遇熱顏色安定性,(c)起霜的傾向,(d)低的熱變形溫度,(e)焦黑的傾向,(f)低衝擊強度及/或不良的熔體流動(高黏度)。除此之外,多種昔知的化合物因爲含有具反應性的基團,所以亦有可能造成熱塑型樹脂的降解。

因此,有必要提供一種阻燃性乙烯芳族樹脂組成物, 以克服上述之一或多種缺點,更特定言之,該組成物具有 下列多項優點(a)不會起霜,(b)良好的紫外光安定性,(c)熱安定性,(d)適當水準的熱變形溫度、衝擊強度與熔體 流動(足夠低的黏度),及(e)對熱塑型樹脂產生最小的降 解。

#### 發明概述

本發明係關於含有一定量之鹵化芳族二元醇和二鹵化

#### 五、發明説明(2)

伸烷基之縮合產物的乙烯芳族樹脂組成物。縮合產物呈現低聚物的型態,一般爲鹵化之聚醚類,並且其在組成物中的量足以提高組成物的阻燃性。產物以不含具反應性的端末基團爲佳。組成物在阻燃性熱塑型模製物件(例如:汽車零件及商用機械護罩)的製造上極具用途。

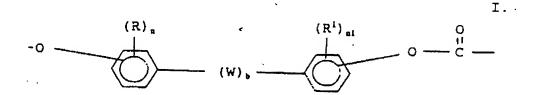
#### 發明詳述

本發明之組成物含有(a)乙烯芳族樹脂,及(b)阻燃劑。乙烯芳族熱塑型樹脂在組成物中的含量最好為基於組成物總重量之50至95重量百分比,並且以其60至90重量百分比為更佳,以其70至80重量百分比為最佳。適宜的乙烯芳族樹脂包括苯乙烯系樹脂(例如:聚苯乙烯、聚(α甲基苯乙烯);耐衝擊聚苯乙烯、苯乙烯丙烯腈共聚物、及乙烯芳族接枝共聚物(例如:丙烯腈一丁二烯一苯乙烯(ABS)接枝共聚物)。組成物亦可含有一定量之他類熱塑型樹脂,例如芳族聚碳酸酯樹脂、多元酯樹脂及一聚、酸醋酸脂或者其掺合物,其中乙烯芳族樹脂的量爲以超克粉、其中乙烯芳族樹脂的量爲以超克粉、其中乙烯芳族樹脂的量爲以超克分比爲更佳,並且芳族聚碳酸酯樹脂、多元酯樹脂及/或聚苯酰樹脂的量爲基於組成物總重量之5至90重量百分比爲更佳。

本發明之芳族碳酸酯樹脂包括聚碳酸酯樹脂及共聚酯碳酸酯樹脂。聚碳酸酯樹脂是習知且熟知之熟塑型樹脂,其通常可購得或者可藉習知的方法容易地製得。這些聚碳

#### 五、發明説明(3)

酸酯,以及其製備的方法,述於.S. Pat. Nos.3,161,615 :3,220,973:3,312,659:3,312,660;3,313,777: 3,666,614及3,393,672,上述文獻均併於本文中以爲參考。聚碳酸酯可以利用多種習知的方法製得,包括界面聚合法,此種方法涉及不少於一種二羥基酚與碳酸酯前驅物間的共同反應。聚碳酸酯樹脂含有至少一個以通式I表示之再熟化結構單元



其中:

R及R<sup>1</sup>分別選自單價烴基、單價烴氧基,及鹵基; W係選自二價烴基,

n及n¹分別選自0至4之整數;且b爲零或者一。

以 R 及 R 1 表示之單價烴基包括烷基、環烷基、芳基、芳烷基及烷芳基。較佳的烷基爲含有 1 至 1 2 約個碳原子者。較佳的環烷基爲含有約 4 至 8 約個環碳原子者。較佳的環烷基爲含有約 4 至 8 約個環碳原子者。較佳的芳基爲含有 6 至 1 2 個環碳原子者,亦即,苯基、酚苯基、及萘基。較佳的芳烷基及烷芳基爲含有 7 至 1 4 約個碳原子者。

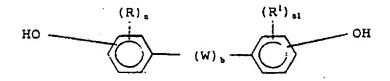
#### 五、發明説明(4)

以R及R¹表示之較佳的鹵基爲氣及溴。

以 W表示之二價烴基包括伸烷基、亞烷基、環伸烷基、與環亞烷基。較佳的伸烷基爲含有 2至約 20個碳原子者。較佳的亞烷基爲含有 1 至約 2 0 個碳原子者。較佳的環伸烷基及環亞烷基爲含有 6 至 1 6 約個環碳原子者。

在聚碳酸酯樹脂之製備中所使用到的二羥基酚可以利用以下的通式表示

II.



其中R、R1、n、n1、W及b的定義如上。

落於式 I 範圍內之二 羥基酚之幾個示範但非限制的實例包括 2, 2-雙(4-羥苯基)丙烷(雙酚 A); 2, 2-雙(3, 5-二溴-羥苯基)丙烷; 2, 2-雙(3-溴-甲基-4-羥苯基)丙烷; 2, 2-雙(3-溴-甲基-4-羥苯基)丙烷; 1, 1-雙(4-羥苯基)環己烷; 1, 1-雙(4-羥苯基)環十二烷; 1, 1-雙(3, 5-二甲基-4-羥苯基)環十二烷; 1, 1-雙(4-羥苯基)癸烷; 1, 4-雙(4-羥苯基)丁烷; 雙(4-羥苯基)甲烷; 4, 4'-硫代二酚; 及雙(4-羥苯基)醚。

其他可用的酚類述於.S. Pat. Nos. 2,998,835、

3,028,365及3,334,154,上 述 文獻 均 併 於 本 文 中 以 爲 參 考

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#### 五、發明説明(5)

碳酸酯前驅物可以是碳醯鹵、碳酸酯、或者是雙鹵甲酸酯。碳醯鹵可以是碳醯溴、碳酶氯、或者其混合物。碳酸酯可以是碳酸二(鹵苯)酯,例如碳酸二(溴苯)酯、及碳酸二(三溴苯)酯;碳酸二(烷苯)酯,例如碳酸二(甲苯)酯;碳酸二萘酯;碳酸氢苯氯萘酯;及碳酸苯甲苯酯。可以使用的雙鹵甲酸酯包括二羟基酚之雙鹵甲酸酯,例如雙酚A及對苯二酚之雙氯甲酸酯;及乙二醇之雙鹵甲酸酯,例如乙二醇、新戊二醇、及聚乙二醇之雙氯甲酸酯。較佳的碳酸酯前驅物爲碳醯氯,亦習稱爲光氣。

用於製備聚碳酸酯的方法有吡啶法、界面聚合法、酯基轉移法、及熔融聚合法。界面聚合法是一種製備聚碳酸酯樹脂的習知方法,此一方法使用兩種不同且不互溶的溶劑介質。溶劑介質之一爲含水鹼性介質。另一溶劑介質爲有機介質,例如二氯甲烷,其與該含水介質不互溶。在界面聚合法中亦使用到分子量調節劑及觸媒,前者可藉鏈終結機制來控制聚碳酸酯之鏈長或分子量。分子量調節劑在本技藝中早爲人所熟知並且包括(但非限於)苯基本身、對位-第三丁基酚、及色滿-I(chronan-I)。所使用的觸媒在本技藝中亦早爲人所熟知並且包括(但非限於)三級胺(例如:三乙胺)、四級銨化物(例如:溴化四乙銨)及四級鏻化物(例如:正丁基三苯基鏻)。

聚碳酸酯之範圍亦包括無規具支鏈之熱塑型聚碳酸酯

### 五、發明説明(6)

,其中支化劑(其一般爲多官能基芳族化合物)是與二羥基酚及碳酸酯前驅物反應。這些多官能基芳族化合物是以微量使用,亦即,能夠有效地提供支化作用的量,並且含有至少三種官能基(其可爲羧基、羥基、羧酸酐、鹵甲醯及其混合物)。這些可作爲支化劑之芳族多官能基化合物之幾個示範但非限制的實例包括苯偏三酸酐、苯偏三酸氯、4-氯甲醯酞酐、苯均四酸、苯均二酸酐、苯六酸、苯六酸酐、苯均三酸及二苯甲酮四羧酸。

共聚酯碳酸酯樹脂在本技藝中早爲人所熟知並且連同其製法共同敘述於U.S. Pat. 3,169,121:4,238,596;4,156,069及4,238,597,上述之文獻均併於本文中以爲參考。

簡而言之,高分子量之熱塑型芳族共聚酯碳酸酯包含位於聚合鏈中之再熟化碳酸酯、羧酸酯及芳族碳環基團內其中至少某些碳酸酯基團及至少某些羧酸酯基團為直接鍵結至芳族碳環基團之環上的碳原子。這些共聚酯碳酸含有位於鏈中之酯鍵及碳酸酯鍵,其中酯鍵的量在約25至約90莫耳百分比的範圍內,並以約35至約80莫耳百分比爲較佳。舉例而言,5莫耳雙酚A可以和4莫耳異煅酶二氯及1莫耳光氣完全反應而得到含有80莫耳百分比酯鍵之共聚酯、碳酸酯。

這些共聚酯碳酸酯可以藉界面聚合法容易地製得,參與反應的反應物爲(i)至少一種二羟基酚,(ii)碳酸酯前驅物,(iii)酯前驅物。二羟基酚及碳酸酯前驅物爲前述

#### 五、發明説明(7)

的類型。酯前驅物可以是雙官能基之羧酸或者是其酯生成之具反應性的衍生物(以此爲較佳),例如,醯基二氯,如異酞醯二氯、對酞醯二氯、及其混合物。. S. Pat. No. 3,169,121提出幾個可用的雙官能基酸。多元酯可以是脂芳族,或者是具有脂芳族特性者。多元酯的特徵在於其具有位於聚合鏈中之再熟化酯單元,亦即鍵結至烴基或者經取代之烴基之碳原子上的羧酸酯基團。

本發明所使用之較佳的多元酯通常含有不少於一個以下列通式表示之再熟化結構單元:

III.

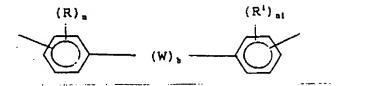
其中R2及R3分別選自二價烴基或者經取代之二價烴基。

如果是脂族多元酯,則 R²及 R³分別選自二價 C脂族烴基或者經取代之二價脂族烴基。二價脂族烴基包括伸烷基、伸烯基、亞烷基、環伸烷基、環亞烷基及環伸烯基。較佳的伸烷基為含有 2至約 20個碳原子者。較佳的亞烷基為含有 1至約 20個碳原子者。較佳的伸烯基為含有 2至約 20個碳原子者。較佳的環伸烷基、環亞烷基及環伸烯基為含有約 4至約 8個環碳原子者。經取代之二價脂族烴基為上述之二價脂族烴基,其並含有至少一個取代基,並且以一至約三個取代基為較佳。較佳的取代基爲鹵素、硝基、及胺基

適合於本發明中使用之芳族多元酯通常含有至少一個 式子皿之再熟化結構單元,其中 R<sup>2</sup>及 R<sup>3</sup>分別選自二價芳

#### 五、發明説明(8)

基或者經取代之二價芳基。以R²及 R³表示之二價芳基包括伸苯基、經取代之伸苯基、聯伸苯基、經取代之聯伸苯基、伸菜基、經取代之申菜基、及以下列通式表示之基團 IIIa



其中R、R1、W、n、n1及b之定義如上。

最具用途的芳族多元酯爲其中之R<sup>3</sup>爲伸苯基且其中之R<sup>2</sup>爲以式子Ⅲ a表示之基團者。

脂芳族多元酯爲其中之R<sup>2</sup>或R<sup>3</sup>中之一者爲二價芳基且R<sup>2</sup>或R<sup>3</sup>中之一者爲二價脂基者。較佳的脂芳族多元酯爲其中之R<sup>2</sup>是二價脂基或者是經取代之二價脂基且R<sup>3</sup>是二價芳基或者是經取代之二價芳基者。

最具用途之脂芳族多元酯中的一類爲聚伸烷基對酞酸酯或者聚伸烷基異酞酸酯。 這些類型的多元酯含有至少一個以下列通式表示之再熟化結構單元

IIIb

其中 m 為數值 2至約 4之整數。最佳之式子 IIIb的多元酯為聚伸乙基對煅酸酯及聚(1,4-伸丁基對酞酸酯)。

最具用途之脂芳族多元酯的另一類型爲多元酯共聚物或者共聚酯,其可包含(但非限於)以下之反應產物:(a)

#### 五、發明説明(9)

包含1,4-環己烷二甲醇之乙二醇部份與包含對酞酸、異酞酸或其混合物之酸部份:或(b)包含1,4-環己烷二甲醇與乙二醇之乙二醇部份,其中乙二醇部份中之1,4-環己烷二甲醇對乙二醇的莫耳比爲約4:1至約1:4,與包含對酞酸、異酞酸或其混合物之酸部份。

這些類型的共聚酯可以利用本技藝中所熟知的程序製得,例如利用實質上如同 U.S.Pat. No. 2,901,466所示之縮合反應製得,此一文獻並併於本文中以爲參考。更特定言知,酸或者酸之混合物或芳族二羧酸或酸之烷酯(例如:對酞酸二甲酯)是與二羥基醇一同載入容器並加熱至足以引發共聚物之縮合反應之溫度,例如,175-225℃。 其後溫度即昇至約250至300℃,並施以真空處理,縮合反應即在此一條件下持續進行直到實質上已完成。

縮合反應可以使用觸媒來促進,至於選用何種觸媒則須視反應物的性質而定。本文所使用的多種觸媒在本技藝中早已爲人所熟知並且因爲數量過多而無法一一述及。一般而言,如果使用二羧酸之烷酯,則觸媒以酯交換型態的觸媒爲較佳。如果是游離酸和游離乙二醇之間的反應,則觸媒通常是在預縮合反應已進行之後方予加入。

反應通常是在過量乙二醇的存在下起始並且最初是加熱至足以引發預縮合反應之溫度,然後再將過量的乙二醇 蒸發。整個反應是在惰性氣壓下利用攪拌來進行。溫度的 調昇可以在施用或者不施用真空的條件下方便地操控。當 溫度進一步地調昇時,壓力可以有效地大幅降低且縮合反

#### 五、發明説明(10)

應仍可持續進行直到達致所欲的聚合度。產物在此一步驟可視爲已完成或者其可依據熟知的技術作進一步的固相聚合反應。由是,高單體縮合產物可加以冷卻、粉碎、並在低於其熔點的溫度下加熱,因而避免了固體顆粒的凝結。固相聚合反應持續進行直到達致所欲的聚合度。固相聚合反應的最終步驟是在溫度高到足以達致所欲之聚合度的條件下進行時,此種降解作用經常發生)。該固相法最好是在常壓或高度減壓之惰性氣壓下利用攪拌來進行。

這些共聚酯在溫度約爲25℃之60/40酚/四氯乙烷或 其他類似溶劑中測得之視黏度通常不低於約0.4 d1/,並 且其在264p.s.i.下的熱變形溫度爲約60℃至約70℃。只 要1,4-環己烷二甲醇對乙二醇的莫耳比爲約1:4至4:1, 共聚酯(b)之乙二醇部份中之1,4-環己烷二甲醇與乙二醇 的相對量即可有所變化以提供具有位於例舉範圍內之適宜 熱變形溫度及其他適宜性質的多元酯共聚物。

在前文述及之類型的共聚酯中有一種極具用途的共聚酯,其中乙二醇部份中之乙二醇的量較1,4-環己烷二甲醇者為高,例如高於約50/50並以約70莫耳乙二醇對30莫耳1,4-環己烷二甲醇為最佳,並且酸部份為對酞酸。此一類型的較佳共聚酯為Eastman Chemical Co.以商標名KODARPETG 6763 販售之商品。較佳的共聚酯係衍生自以1,4-環己烷二甲醇作為乙二醇部份及以異酞酸與對酞酸生成的混

#### 五、發明説明(11)

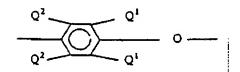
合物作爲酸部份。此種型態的共聚酯可由 Eastman Chem-ical Co.以商標名KODAR A150 購得。

如果此處使用聚碳酸酯與多元酯的掺合物,則多元酯對聚碳酸酯的比率可在廣泛的範圍內變化。一般而言,以含有5約至約85重量百分比芳族碳酸酯樹脂及約85至約5重量百分比多元酯之組成物爲較佳,並以含有約10至約70重量百分比多元酯之組成物爲含有約20至約60重量百分比芳族碳酸酯樹脂及約60至約20重量百分比多元酯者。芳族碳酸酯樹脂之重量百分比係基於組成物中存在之芳族碳酸酯樹脂及多元酯樹脂的總量而言。同樣地,多元酯之重量百分比係基於本組成物(意指,多元酯/芳族碳酸酯掺合物)中存在之多元酯樹脂及芳族碳酸酯樹脂的總量而言。

聚苯醚(PPE)樹脂在本技藝中早爲人所熟知,其並述於 Allan Hay 之 U.S. Patents 3,306,874; 3,306,875及3,432,469; Gelu Stamatoff 之 U.S. Patents 3,257,357及3,257,358; Dwain M. White 等人之 U.S. Patent 4,806,602; 與 Sterling B. Brown等人之 U.S. Patent 4,806,297,上述文獻均併於本文中以爲參考。聚苯醚之均聚物及共聚物亦在本發明之範圍內。

較佳的PPE 樹脂爲包含多個下式之結構單元的均聚物 與共聚物

#### 五、發明説明(12)



其中各個Q¹分別選自鹵素、一級或二級低碳烷基、苯基、鹵烷基、胺烷基、烴氧基、或鹵基烴氧基,且其中鹵原子與氧原子間隔至少兩個碳原子;且各個Q²如同Q¹所定義者,其分別選自氫、鹵素、一級或二級低碳烷基、苯基、鹵烷基、、烴氧基、或鹵基烴氧基。

適宜之一級低碳烷基的例子有甲基、乙基、正丙基、正丁基、異丁基、正戊基、異戊基、2-甲丁基、正己基、2、3-二甲丁基、2-、3-或4-甲戊基、及對應之庚基。二級低碳烷基的例子有異丙基、第二丁基及3-戊基。最好是所有的烷基均爲直鏈,而非具有支鏈。一般而言,各個Q¹爲烷基或者苯基(並以C14烷基爲佳),並且各個Q²爲氫。最佳的聚苯醚爲包含衍生自2,6-二甲基酚之單元者。在某些例子中,包含衍生自2,6-二甲基酚及2,3,6-三甲基酚之單元的PPE共聚物亦佳。

PPE樹脂可以含有某些對諧如分子量、熔體黏度、或衝擊強度具改質能力的部份。舉例而言,乙烯單體及乙烯基芳族化合物可以接枝至PPE聚合物,這一部份述於Sterling B. Brown 等人之專利申請案(Attorney Docket Number RD-19372, U.S. Serial No. 351,903, filed May 15,1989),其整個內容並併於本文中以爲參考。

在另一個例子中,亦可使用經偶合之PPE聚合物,其中

#### 五、發明説明(13)

偶合劑是與兩個PPE鏈之羥基反應以製得較高分子量之聚合物。

本 發 明 之 PPE樹 脂 通 常 具 有 約 20,000至 80,000之 重 量 平 均 分 子 量 (由 凝 膠 渗 透 層 析 法 測 得 )。

除此之外,其可由本技藝中習知的方法製得:例如,適宜之單羥基芳族化合物在基於銅、錳、或鈷之觸媒的存在下經氧化偶合而得。

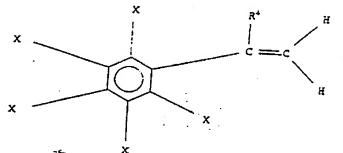
較佳的熱塑型樹脂爲經橡膠改質之單亞乙烯芳族化合物,例如乙烯芳族化合物-丙烯腈-二烯橡膠接枝共聚物。

經橡膠改質之單亞乙烯芳族樹脂包含(a)經橡膠改質之單亞乙烯芳族接枝共聚物及(b)未經接枝之剛性共聚物,並且通常是由單亞乙烯芳族單體與一或多種共聚單體形成之混合物在一或多種橡膠聚合基材的存在下經接枝及內離基質或之間性(共)聚合物之分離基質或者者與得不可以和經橡膠改質之單亞乙烯芳族接枝聚合物共同製得,視存在之橡膠量而定。樹脂亦可若剛性單亞乙烯芳族接枝共聚物的溶合製得。與型上,經歷歷改質之樹脂所包含之經經歷過一次與其10至95重量百分比爲更佳,以其15至90重量百分比爲較佳,以其10至95重量百分比爲更佳,以其15至

#### 五、發明說明(14)

85重量百分比爲最佳。

可以使用之單亞乙烯芳族單體包括苯乙烯、 α -甲基苯乙烯、 鹵基苯乙烯(意指二溴苯乙烯)、核心環上具單或二烷基、烷氧基或羥基取代基之單亞乙烯芳族單體(意指乙烯基甲苯、乙烯基二甲苯、丁基苯乙烯、對羥基苯乙烯或甲氧基苯乙烯)或其混合物。所使用之單亞乙烯芳族單體一般是以下式敘述:

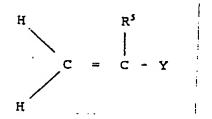


其中X係選自氫、1至5個碳原子之烷基、環烷基、芳基、烷芳基、芳烷基、烷氧基、芳氧基、及鹵素。R<sup>4</sup>係選自氫、1至5個碳原子之烷基及鹵素(例如溴及氯)。經取代之乙烯芳族化合物的例子包括苯乙烯、4-甲基苯乙烯、3,5-二乙基苯乙烯、4-正丙基苯乙烯、α-甲基苯乙烯、α-甲基苯乙烯、二氯苯乙烯、二氯苯乙烯、四氯苯乙烯、 這些化合物的混合物等。所使用之較佳的單亞乙烯芳族單體爲苯乙烯及/或α-甲基苯乙烯。

可以和單亞乙烯芳族單體一起使用的共聚單體包括丙烯腈、甲基丙烯腈、經C1至C8烷基或芳基取代之丙烯酸酯或經C1至C8烷基、芳基或鹵芳基取代之甲基丙烯酸酯、丙烯酸、甲基丙烯酸、衣康酸(itaconic acid)丙烯醯胺、N

#### 五、發明説明(15)

-取代之丙烯醯胺或甲基丙烯醯胺、馬來酐、馬來醯亞胺 、N-烷基、芳基或者經鹵芳基取代之馬來醯亞胺、縮水甘油(甲基)丙烯酸酯、羥基烷基(甲基)丙烯酸酯或其混合物 。丙烯腈、經取代之丙烯腈、或者丙烯酸酯一般是以下式 表示:



其中 R<sup>5</sup>可以選自與先前定義之 R<sup>4</sup>相同的基團且 Y係選自氰基及羰基烷氧基且其中羰基烷氧基之烷氧基含有一至約十二個碳原子。此種單體的實例包括丙烯腈、乙基丙烯腈、甲基丙烯腈、α-氯基丙烯腈、α-溴基丙烯腈、丙烯酸甲酯、甲基丙烯酸甲酯、丙烯酸乙酯、丙烯酸甲酯、丙烯酸异丙酯及其混合物。較佳的單體爲丙烯酸丙酯、丙烯酸酯爲丙烯酸乙酯及甲基丙烯酸甲酯。丙烯酸酯(當被包括在內時)與苯乙烯或丙烯腈組合使用亦佳。

經橡膠改質之接枝共聚物包含(i)橡膠基材,及(ii)接枝至橡膠基材之剛性聚合叠接物(super-strate)部份。橡膠基材在接枝共聚物中的量最好爲基於接枝共聚物總重量的5至85重量百分比,並以其10至80重量百分比爲較佳,以20其至70重量百分比爲最佳;並且剛性叠接物的量最好爲基於接枝共聚物總重量的15至95重量百分比,並以其

#### 五、發明説明(16)

20至90重量百分比爲較佳,以其30至80重量百分比爲最佳

對高橡膠接枝之乳化樹脂而言,橡膠含量爲基於經橡膠改質之樹脂總重量的50至85%重量比。對本體聚合而言,橡膠含量爲基於經橡膠改質之樹脂總重量的4至40%重量比。對未經接枝之剛性共聚物(例如苯乙烯丙烯腈共聚物)與乳化之高橡膠接枝(HRG)共聚物(例如丙烯腈丁二烯苯乙烯接枝共聚物)之掺合物而言,負載之橡膠量通常爲基於經橡膠改質之樹脂總重量的10至40%橡膠。

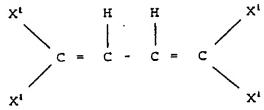
作為基材之橡膠聚合物的例子包括:共軛二烯、二烯 與苯乙烯、丙烯腈、甲基丙烯腈或者丙烯酸 C1至 Ca烷酯形成的共聚物,其含有不少於 50% (最好不少於 65% 重量比) 共軛二烯、聚異戊二烯或其混合物;烯烴橡膠,指乙烯丙烯共聚物 (EPR)或者乙烯丙烯非共軛二烯 (EPDM);矽酮橡膠;或者丙烯酸 C1至 Ca烷酯之均聚物或其與丁二烯及/或苯乙烯形成的共聚物。丙烯酸聚合物亦可含有高至 50% 之一或多種多官能基交連劑,例如伸烷二醇與二(甲基)丙烯酸多元酯二(甲基)丙烯酸酯、二乙烯基苯、三乙烯基苯、丁二烯、異戊二烯,及視須要選用之可接較形成的基本、五二烯丙酯、厚丁烯二酸二烯丙酯、反丁烯二酸二烯丙酯、阿丁烯二酸二烯丙酯、阿丁烯二酸二烯丙酯或道些試劑的混合物。

二烯橡膠最好是聚丁二烯、聚異戊二烯及丁二烯與高

#### 五、發明説明(17)

至35%以重量計之共聚單體(例如苯乙烯、丙烯腈、甲基丙烯酸甲酯或丙烯酸 C1-Ce烷酯)經水相自由基乳化聚合反應而成的共聚物。丙烯酸酯橡膠可以是經過交連、實質爲丙烯酸 C1-Ce烷酯(特別是丙烯酸 C2-Ce烷酯)之微粒乳化共聚物,並可視須要與高至15%以重量計之共聚單體(例如苯乙烯、甲基丙烯酸甲酯、丁二烯、乙烯基甲醚或丙烯腈)及視須要與高至5%以重量計之多官能基交連性共聚單體(例如二乙烯基苯、乙二醇與雙丙烯酸形成的酯類、雙丙烯酸胺、磷酸三烯丙酯、存橼酸三烯丙酯、丙烯酸或甲基丙烯酸之烯丙酯、三聚氟尿酸三烯丙酯、三聚異氯尿酸三烯丙酯)掺合。二烯橡膠與丙烯酸烷酯橡膠與具有所謂核心/外鞘結構(例如二烯橡膠核心及丙烯酸酯外鞘或反是)之橡膠形成的混合物亦適宜。

經常使用於製備接枝聚合物之橡膠基材的特定共軛二烯單體,其一般是以下式表示:



其中 X<sup>1</sup> 係選自氫、含一至五個碳原子之烷基、氨或溴。可以使用之二烯的例子有丁二烯、異戊二烯、1,3-庚二烯、甲基-1,3-戊二烯、2,3-二甲基丁二烯、2-乙基-1,3-戊二烯、1,3-及2,4-己二烯、經氨及溴取代之丁二烯(例如二氯丁二烯、溴丁二烯、二溴丁二烯、其混合物)等。較佳的共軛二烯爲1,3-丁二烯。

#### 五、發明説明(18)

如前所述,基材聚合物最好是共軛二烯聚合物,例如 聚丁二烯、聚異戊二烯、或者是共軛二烯之共聚物,例如 丁二烯苯乙烯、丁二烯丙烯腈、或其類似物。橡膠聚合基 材部份必須具有低於約0℃之玻璃轉移溫度(Tg)。

前述用於製備單亞乙烯芳族接枝聚合物之一或多種橡膠聚合物形成的混合物,或者揭示於本文之一或多種經像膠改質之單亞乙烯芳族接枝聚合物形成的混合物亦可使用。除此之外,橡膠亦可包含嵌段或者無規共聚物。使用於本發明且經簡單之光線透射法或者毛細管流體動力層析法(CHDF)測得的橡膠顆粒尺寸可以具有選自下列之一的平均顆粒尺寸來述敘:基於乳化之經聚合之橡膠乳漿爲0.05至1.2微米,並以0.2至0.8微米爲佳,經本體聚合之橡膠基材(其亦包括經接枝之單體吸留物)爲0.4至10微米,並以0.4至1.5微米爲佳。橡膠基材最好是微粒、經高度交連之二烯或丙烯酸烷酯橡膠,並且最好具有高於70%之凝膠含量。

較佳之接枝疊接物包括苯乙烯與丙烯腈之共聚物、 a
-甲基苯乙烯與丙烯腈之共聚物及甲基丙烯酸甲酯聚合物或具有高至50%以重量計之丙烯酸 C1-Ce烷酯、丙烯腈或苯乙烯之共聚物。單亞乙烯芳族接枝共聚物的特定實例包括(但非限於)下列:丙烯腈丁二烯苯乙烯(ABS)、丙烯腈苯乙烯丙烯酸丁酯(ASA)、甲基丙烯酸甲酯丙烯腈丁二烯苯乙烯(MABS)、丙烯腈乙烯丙烯非共軛二烯苯乙烯(AES)

。 未 經 接 枝 之 剛 性 聚 合 物 ( 典 型 上 不 含 橡 膠 ) 爲 苯 乙 烯 、 α

#### 五、發明説明(19)

-甲基苯乙烯、核心經諸如 ρ -甲基苯乙烯、丙烯酸甲酯、甲基丙烯酸甲酯、丙烯腈、甲基丙烯腈、馬來酐、N-取代之馬來醯亞胺、乙酸乙烯酯或其混合物取代之苯乙烯等之樹脂、熱塑型聚合物。苯乙烯/丙烯腈共聚物、α-甲基苯乙烯/丙烯腈共聚物及甲基丙烯酸甲酯/丙烯腈共聚物爲其中較佳者。

未經接枝之剛性共聚物早爲人習知並且可藉自由基聚 合反應(特別是藉乳化、懸浮、溶液或整體聚合反應)製得 。其數均分子量最好在20,000至200,000。

單亞乙烯芳族樹脂之經接枝之剛性疊接物的數均分子 量被設定在20,000至350,000之範圍內。單亞乙烯芳族單 體對第二及視須要選用之第三單體的比率可由90/10至50 /50,並以80/20至60/40爲佳。第三單體可以視須要替 代0至50%第一及第二單體中的一者或兩者。

這些經橡膠改質之單亞乙烯芳族接枝聚合物可以利用本體法、乳化法、懸浮法、溶液法或組合之方法(例如本體法-懸浮法、乳化法本體法、本體法溶液法)或本技藝熟知的其他技術施以聚合。除此之外,這些經橡膠改質之單亞乙烯芳族接枝共聚物可以利用連續法、半批次法或批次法製得。

組成物最好含有基於組成物總重之3至40重量百分比的阻燃劑,並以其7至25重量百分比爲較佳,以其12至20重量百分比爲最佳。

阻燃劑是鹵化芳族二元醇(以溴化芳族二元醇爲佳)與

#### 五、發明説明(20)

二鹵化伸烷基組成物的縮合產物。溴化芳族二元醇最好是 溴 化 雙 酚 、 並 以 四 溴 雙 酚 爲 較 佳 。 二 鹵 化 伸 烷 基 組 成 物 最 好 是 C<sub>1</sub>-C<sub>18</sub>(烷 基 部 份 有 一 至 十 八 個 碳 原 子 )單 鹵 化 烷 與 C1-C1a二 鹵 化 伸 烷 基 生 成 的 混 合 物 。 C1-C1a單 鹵 化 烷 最 好 是 C <sub>1</sub> - C 4 烷 基 溴 , 並 以 甲 基 溴 爲 較 佳 。 C 1 - C 1 a 二 鹵 化 伸 烷 基最好是 C1-C4伸烷基二溴,並以伸乙基二溴爲較佳。二 鹵 化 伸 烷 基 組 成 物 最 好 包 含 基 於 二 鹵 化 伸 烷 基 組 成 物 總 重 之 5至 95重 量 百 分 比 之 單 鹵 化 烷 , 並 以 10至 40重 量 百 分 比 爲 較 佳 , 以 2 0 至 3 5 重 量 百 分 比 爲 最 佳 ; 並 且 最 好 包 含 基 於 二 鹵 化 伸 烷 基 組 成 物 總 重 之 5至 95重 量 百 分 比 之 二 鹵 化 伸 烷基, 並以60至90重量百分比爲較佳,以65至80重量百分 比爲最佳。存在於二鹵化伸烷基組成物中之單鹵化烷與二 鹵 化 伸 烷 基 的 各 別 莫 耳 比 最 好 介 於 1: 9 與 2: 1之 間 , 並 以 介 於 : 1與 1.5 : 1之 間 爲 較 佳 , 以 介 於 1 : 3與 1: 1之 間 爲 最佳。低聚性阻燃劑具有之數均分子量最好介於1000克/ 莫耳與8000克/莫耳之間,並以介於1300克/莫耳與6000 克 / 莫 耳 之 間 爲 較 佳 , 以 介 於 1500克 / 莫 耳 與 3000克 / 莫 耳之間爲最佳。單鹵化烷最好爲下式之化合物:

X2-R6

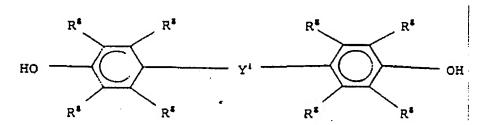
其中 X<sup>2</sup>爲鹵素,其最好選自 級及溴,並以溴爲最佳;並且 R<sup>6</sup>爲(具支鏈或不具支鏈)C<sub>1</sub>-C<sub>18</sub>烷基,並以C<sub>1</sub>-C<sub>4</sub>烷基爲佳,以選自甲基及乙基爲更佳。伸烷二鹵最好爲下式之化合物:

X 2 - R 7 - X 2

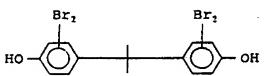
#### 五、發明説明(21)

其中 X<sup>2</sup>之定義如上:且 R<sup>7</sup>是具有 C<sub>1</sub>-C<sub>18</sub>碳原子之伸烷基二價基團,並以 C<sub>1</sub>-C<sub>8</sub>碳原子為較佳,以選自伸乙基及二價基團為最佳。

鹵化芳族二元醇以溴化芳族二元醇爲較佳,並且以下 式之溴化雙酚爲更佳



其中各個R®分別選自氫原子、氦原子、溴原子及含有1至5個碳原子之烷基,但其前題是至少一4個R®基團爲氦或溴原子,並且以溴原子爲較佳:且其中Y¹表示單鍵或選自-0-、-S-、\_-S02-、-S0-、-C0-、含有1至10個碳原子之伸烷基及亞烷基等二價基團及含氧、矽、硫或氮之脂族烴基、例如-0R®0-、--OR®0R®0-、-SR®S-、-SR®SR®S-、-OSiR®20--OSiR®20-、-O2CR®C02-、-C02R®02C-、-S0R®S0-、-S02R®S02-,其中R®爲C1-C10二價脂族烴基。最好上述之二元醇中至少有4個R®基團爲溴。Y¹以C3基團爲佳。較佳之溴化雙酚爲四溴雙酚A,其可以下列之通式表示:



並以下式爲較佳

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# ( 請先閱讀背面之注意事項再填寫本頁 )

阻燃劑可以下列通式表示:

$$R^{6}-O \xrightarrow{\mathbb{R}^{8}} R^{8} \xrightarrow{\mathbb{R}^{8}} R^{8} \xrightarrow{\mathbb{R}^{8}} \mathbb{R}^{8} \bigcirc -R^{7}-O \xrightarrow{\mathbb{R}^{8}} \mathbb{R}^{8} \xrightarrow{\mathbb{R}^{4}} \mathbb{R}^{8} \xrightarrow{\mathbb{R}^{4}} \mathbb{R}^{8} \xrightarrow{\mathbb{R}^{4}} \mathbb{R}^{9}$$

其中R<sup>6</sup>、R<sup>7</sup>及R<sup>8</sup>定義如上,且n<sup>2</sup>以選自1至12爲佳,以選自1至5爲較佳,並且以選自2至4爲最佳。阻燃劑可以經由任何適宜之縮合反應(包括醚類溶劑存在下之反應)製得。因爲阻燃劑是以烷基作端末包封,所以得以避免具反應性之端末基團引起的問題。

組成物亦可含有阻燃協合劑,適宜之協合劑包括錦化物、硼酸鋅、鋇、有機磷酸鹽、鉬組份、偏硼酸鹽、水合氧化鋁、氧化鋯及聚磷酸銨。適宜之錦化物包括 Sb203、Sb2S3、K3Sb、Na3Sb及Li3Sb。協合劑在熱塑型組成物中的量最好爲基於組成物總重之1至15重量百分比,並以2至10重量百分比爲較佳,以5至9重量百分比爲最佳。

組成物亦可含有液滴抑制劑(例如四氟乙烯聚合物), 其含量以基於組成物總重之 0.1至 5重量百分比爲佳。依據 本發明,適宜之四氟乙烯聚合物爲具有 65-76%重量比(以 70-76重量比爲佳)之氟含量者,其實例有聚四氟乙烯、四 氟乙烯/六氟丙烯共聚物、四氟乙烯/1,1-二氟乙烯共聚 物及含有少量之無氟且可共聚之乙烯系不飽和單體的四氟

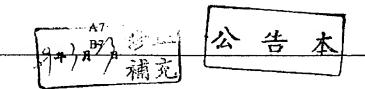
#### 五、發明説明(23)

乙烯共聚物。此類聚合物可由以下得知:"Vinyl and Related Polymers", John Wiley&Sons, Inc., New York, 1952, page 484-494: "Fluorpolymers", Wiley- Interscience, New York, 1972; "Encyclopedia of Polymer Science, New York, 1972; "Encyclopedia of Polymer Science and Technology", Interscience Publishers, New York, Volume 13, 1970, page 623-654; "Modern Plastics Encyclopedia", 1970-1971, Volume 47, No. 10A, October 1970 McGraw-Hill, Inc., New York, page 134, 138及; "Modern Plastics Encyclopedia", 1975-1976, October 1975, Volume 52, No. 10A, McGraw Hill, Inc., New York, page 27, 28及及.S. Pat. Nos. 3, 671, 487, 3, 723, 373及3,838,092。

以下實例說明組成物中阻燃劑所欲之性質。

#### 實例

製得含有20.4份以重量計(pbw)之四溴雙酚A/甲基溴/伸乙基二溴縮合產物低聚物、9 pbw Sb2O3、6pbw氯化聚乙烯(CPE)及100pbw 丙烯腈一丁二烯一苯乙烯接枝共聚物之ABS接枝共聚組成物。該組成物亦含有潤滑劑及著色劑。實例1之阻燃劑爲下式之化合物:



## 五、發明説明(24)

實例1之組成物不會發生起霜之現象、並具有25呎-磅之加德納爾衝擊(Gardner impact)、4.4呎磅/吋之缺口衝擊、氙電弧試驗300小時下之顏色轉移(dE)僅1.66、400°F及1000/秒下之熔體黏度爲3451泊且1/8"及264psi下之熱變形溫度爲159°F、60密耳(mil)下具有阻燃水準、2806瓦-小時/平方米下HPUV之爲1.57、並且在加工過程中無炭之生成。

實例2使用下式之阻燃劑

於 ABS組成物中,並具有良好之顏色、無起霜、良好的抗紫外光性、UV(dE)=1.19、60密耳下之UV94=V0、90密耳下之UL94=5V、4.1呎磅/吋之缺口衝擊、18呎-磅之加德納爾衝擊、1/8"及264psi下之HDT為169°F、400°F及1000/秒下之熔體黏度爲3559泊。

實例3是以高衝擊性聚苯乙烯替代上述實例1之組成物中的ABS並且其在60密耳下之UL-94爲 V-2,且在250密耳下爲 VO。

實例4是以雙酚聚碳酸酯/ABS 掺合物替代質例1之ABS並且其在60密耳下之UL-94評價爲V-0、並具有9.7呎磅/吋之缺口衝擊且500°F及1000/秒下之熔體黏度爲1405泊。

A8 B8 C8 D8 90 4 -6 \*\* -

#### 六、申請專利範圍

附件1(a):

第.85101671號 專 利 申 請 案

中文申請專利範圍修正本

民國90年4月修正

請先閱讀背面之注意事項再填寫本頁

- 1. 一種阻燃熱塑型組成物,其包含:
- (a)基於組成物總重之60至97重量百分比之乙烯芳族樹脂,及
- (b)基於組成物總重之3至40重量百分比之阻燃劑, 該阻燃劑爲以下通式之化合物:

其中各個 R®分別爲 C1至 C18烷基,各個 R®分別選自 溴、氯、氫及 C1至 C5烷基,但其前題是各個雙酚部 份之至少一個 R®基團爲溴,各個 R7爲具有 1至 18個 碳原子之二價基團,各個 Y¹分別選自 -0-、-S-、 -SO2-、-SO-、-CO-、具有 1至 10個 碳原子之伸烷基

及亞烷基,且n²選自1至12。

- 2. 如申請專利範圍第1項之組成物,其中,該組成物進一步包含丙烯腈一二烯一乙烯芳族接枝共聚物。
- 3. 如申請專利範圍第2項之組成物·其中,該接枝共聚物爲丙烯腈-丁二烯-苯乙烯接枝共聚物。
- 4. 如申請專利範圍第1項之組成物,其中,該阻燃劑係以以下之通式表示:

#### 六、申請專利範圍

其中 n²選 自 1至 12。

- 5. 如申請專利範圍第1項之組成物,其中,該組成物進一步包含1至15重量百分比之銻化合物。
- 6. 如申請專利範圍第1項之組成物,其中,該乙烯芳族樹脂是經衝擊改質之苯乙烯聚合物。

# 公告本

附件三:第 85101671 號專利申請案中文說明書修正頁 民國 88 年 10 月呈

申請	日期	85	年	2	月	10	B
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( y	人上各村	制由.	本局填註)
		冬年	簽明 專利 説明書
發明	中	文	含有鹵化芳族二元醇和二鹵化伸烷基之縮合産物的乙烯芳族樹脂 成物
-、77 名稱	英	文	Vinyl aromatic resin compositions containing condensation product of halogenated aromatic diel and an alkylene dihalide
	姓	名	<ul> <li>(1) 湯姆士・克里夫蘭 Cleveland, Thomas Benson</li> <li>② 唐諾・古利奇 Kulich, Donald Michael</li> <li>(3) 安瑞克・特遇 Termine, Enrico J.</li> </ul>
<b>₹</b> \$.88	國	籍	(1) 美國 Ø 美國 (3) 美國 (1) 美國西維吉尼亞州・帕克斯堡・第十街三一六 號
- 、發明 - 、創作 人	住、	医所	316 10th Street, Parkersburg, West Virginia 26101, U
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	姓 (名:	名 稱)	deneral precent company
	國	籍	(1) 美國
三、申請人	住、,		
	代技	<b>人</b> 名	(1) 雷・柴斯金 Chaskin, Jay L.

線

附件 2:第 85101671 號專利申請案中文說明書修正頁 民國 89 年 3 月呈

五、發明說明 (

公告本

發明背景

發明範疇

本發明係關於乙烯芳族樹脂組成物並且更特定言之係關於阻燃性乙烯芳族樹脂組成物。

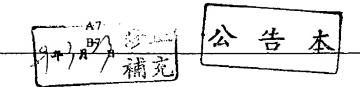
#### 相關技藝的敘述

溴化阻燃劑及其用於阻燃乙烯芳族樹脂(例如丙烯腈
一丁二烯一苯乙烯(ABS)接枝共聚物)的用途早爲人所習知
。更特定言之,ABS接枝共聚組成物中使用經溴化之雙
酚A即爲一例。然而,此種阻燃組成物因爲阻燃劑的掺入
而有以下之一或多種缺點,即(a)不良的紫外光安定性,(b)不良的遇熱顏色安定性,(c)起霜的傾向,(d)低的熱變
形溫度,(e)焦黑的傾向,(f)低衝擊強度及/或不良的熔
體流動(高黏度)。除此之外,多種昔知的化合物因爲含有
具反應性的基團,所以亦有可能造成熱塑型樹脂的降解。

因此,有必要提供一種阻燃性乙烯芳族樹脂組成物,以克服上述之一或多種缺點,更特定言之,該組成物具有下列多項優點(a)不會起霜,(b)良好的紫外光安定性,(c)熱安定性,(d)適當水準的熱變形溫度、衝擊強度與熔體流動(足夠低的黏度),及(e)對熱塑型樹脂產生最小的降解。

#### 發明概述

本發明係關於含有一定量之鹵化芳族二元醇和二鹵化



## 五、發明説明(

實例1之組成物不會發生起霜之現象、並具有25呎-磅之加德納爾衝擊(Gardner impact)、4.4呎磅/吋之缺口衝擊、氙電弧試驗300小時下之顏色轉移(dE)僅1.66、400°F及1000/秒下之熔體黏度爲3451泊且1/8"及264psi下之熱變形溫度爲159°F、60密耳(mil)下具有阻燃水準、2806瓦-小時/平方米下HPUV之爲1.57、並且在加工過程中無炭之生成。

實例2使用下式之阻燃劑

於ABS組成物中,並具有良好之顏色、無起霜、良好的抗紫外光性、UV(dE)=1.19、60密耳下之UV94=V0、90密耳下之UL94=5V、4.1呎磅/吋之缺口衝擊、18呎-磅之加德納爾衝擊、1/8"及264psi下之HDT爲169°F、400°F及1000/秒下之熔體黏度爲3559泊。

實例 3是以高衡擊性聚苯乙烯替代上述實例 1之組成物中的 ABS並且其在 60密耳下之 UL-94爲 V-2,且在 250密耳下爲 VO。

實例4是以雙酚聚碳酸酯/ABS 掺合物替代質例1之ABS並且其在60密耳下之UL-94評價爲V-0、並具有9.7呎磅/吋之缺口衝擊且500°F及1000/秒下之熔體黏度爲1405泊。

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#### 六、申請專利範圍

附件1(a): 第85101671號專利申請案 中文申請專利範圍修正本

民國90年4月修正

請先閱讀背面之注意事項再填寫本頁

- 1. 一種阻燃熱塑型組成物,其包含:
- (a)基於組成物總重之60至97重量百分比之乙烯芳 族樹脂,及
- (b)基於組成物總重之3至40重量百分比之阻燃劑, 該阻燃劑爲以下通式之化合物:

$$\mathbb{R}^{4} - O \xrightarrow{\mathbb{R}^{4}} \mathbb{R}^{4} \xrightarrow{\mathbb{R}^{4}} \mathbb{R}^{4} \xrightarrow{\mathbb{R}^{4}} \mathbb{R}^{4} \longrightarrow \mathbb{R}^{4}$$

其中各個R®分別爲C1至C18烷基,各個R®分別選自 溴、氯、氫及C1至C5烷基,但其前題是各個雙酚部 份之至少一個R®基團爲溴,各個 R<sup>7</sup>爲具有1至18個 碳原子之二價基團,各個Y¹分別選自-0-、-S-、 -S02-、-S0-、-C0-、具有1至10個碳原子之伸烷基 及亞烷基,且n²選自1至12。

- 2. 如申請專利範圍第1項之組成物,其中,該組成物進一步包含丙烯腈一二烯一乙烯芳族接枝共聚物。
- 3. 如申請專利範圍第2項之組成物,其中,該接枝共聚物爲丙烯腈-丁二烯-苯乙烯接枝共聚物。
- 4. 如申請專利範圍第1項之組成物,其中,該阻燃劑係以以下之通式表示: